Growth and characterization of cadmium oxalate crystals using agar gel

B P Agarwal, K M Chauhan & Mohan M Bhadbhade*
Department of Physics, Gujarat University, Ahmedabad 380 009
*Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002
Received 9 September 1998; revised 4 January 1999; accepted 1 April 1999

Cadmium oxalate trihydrate crystals have been grown in agar gel at ambient temperatures. The technique of using agar gel for the growth of cadmium oxalate is more successful in reducing nucleation centres than the technique of using silica hydrogel where foreign substances such as LiCl, NaCl, KCl and NH₄Cl are added to modify the initial characteristics of the silica gel. Crystals grown in agar gels were flawless and transparent. Chemical etching proved a high degree of perfection of the crystals.

The crystals were characterized by X-ray diffraction study, thermogravimetric and differential scanning calorimetry analysis.

1 Introduction
There has been constant urge for growing defect-free large single crystals of substances. Of all the techniques for the growth of single crystals, growth of crystals using gel media has found a unique place due to its characteristic of suppression of nucleation centres

Transition metal oxalates are generally synthesized in aqueous media by double decomposition of their soluble salts with alkali metal oxalates or oxalic acid. This procedure results in the immediate precipitation which is highly insoluble in the form of powdered aggregates. Different procedures were used to obtain single crystals of oxalates but without much success

However, growth from gel has proved to be very useful for materials with low solubility including oxalates.

There are not many efforts in the literature on the growth of cadmium oxalate. However, Arora et al. have grown cadmium oxalate using silica gel and used NH₄Cl, NaCl, LiCl, KCl, etc. as foreign impurity to avoid Liesegang ring formation.

The purpose of this paper is to report the growth of cadmium oxalate using agar gel (a carbohydrate polymer derived from seaweeds) where no foreign impregnation of the gel is required for the nucleation control. Against this, in silica gel (in case of cadmium oxalate) nucleation control is achieved only by impregnation of gel using foreign substances

2 Experimental Details
Since growth of cadmium oxalate crystals from pure silica gel leads to the formation of Liesegang ring, the growth of these crystals were tried by using agar gel.

The chemicals used in this study were cadmium chloride BDH, oxalic acid BDH and agar-agar powder (commercial grade). The following general chemical reaction was employed for the growth of these crystals:

\[
\text{CdCl}_2 \cdot \text{H}_2\text{O} + (\text{COOH})_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O} + 2\text{HCl}
\]

The gel solution was prepared by dissolving agar-agar powder in double distilled water at boiling temperature. Solutions of different concentrations ranging from 0.5 to 2% were prepared by dissolving 0.5 gm to 2 gm of agar-agar powder in 100 gm of double distilled water. The gel solutions were transferred to the growth apparatus before setting. Apparatus consists of a U-tube with both ends open, arm length 25 cm and diameter 2.5 cm.

The gel setting period varied from 3 to 6 days depending on the setting condition employed.

Feed solutions were prepared by dissolving cadmium chloride and oxalic acid separately in double distilled water.

Once the gel was set, the feed solutions were carefully poured above the gel. Cadmium chloride solution was added into one arm of the U-tube and oxalic acid to the other arm of the U-tube. It was observed after few days that the crystals of CdC₂O₄·3H₂O are formed.

Experiments were carried out with feed solutions of different molarity (0.5 to 1.5 M) and different concentration of gel (0.5 to 2%) to find optimum condition for the growth of crystals.

The growth period varied widely in the range of 30-90 days depending on the composition and molarity of feed
solutions and gel concentration. The results are summarized in Table 1.

3 Results and Discussion

3.1 Crystal quality

It is obvious from Table 1 that the quality and size of the crystals vary with concentration of gel as well as with concentration of feed solutions. The optimum condition for the growth of best crystals was 1.3% gel and 1.5 M solutions of cadmium chloride and oxalic acid. Typical gel grown crystals of cadmium oxalate are shown in Fig.1.

As-grown crystals are very transparent and inclusion free which is evident from Fig. 1. Optical microphotographs of the crystal faces were taken by using Andhra Scientific Co metallurgical microscope. One such case of as-grown face of the crystal is shown in Fig.2. Growth layers are clearly seen. Concentrated nitric acid and water in ratio 1:15 is found to produce good etch pits. A typical etched pattern on (001) face is shown in Fig.3. Average dislocation density was found to be $10^4\text{Cm}^{-2}$. This indicates that crystals are fairly defect-free.

![Fig. 1 - Some of the crystals of cadmium oxalate grown from agar-agar gel (mm scale)](image1)

![Fig. 2 - As grown face of the crystal of cadmium oxalate \times 25](image2)

<table>
<thead>
<tr>
<th>% of gel solution</th>
<th>Concentration of feed solutions</th>
<th>Observations</th>
<th>Growth Period</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cadmium Chloride</td>
<td>Oxalic Acid</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.5M to 1M</td>
<td>1M</td>
<td>Many nuclei formed. Crystals were very thin, small and translucent. Maximum crystal dimension $3 \times 2 \times 1 \text{ mm}^3$.</td>
</tr>
<tr>
<td>0.7</td>
<td>0.5M to 1M</td>
<td>1M</td>
<td>As above, no significant change</td>
</tr>
<tr>
<td>0.9</td>
<td>0.5M to 1M</td>
<td>1M</td>
<td>As above, no significant change</td>
</tr>
<tr>
<td>1</td>
<td>1M</td>
<td>1M</td>
<td>Improvement in size. Maximum crystal dimension $6 \times 5 \times 2 \text{ mm}^3$.</td>
</tr>
<tr>
<td>1.1</td>
<td>1M</td>
<td>1M</td>
<td>As above, no significant change</td>
</tr>
<tr>
<td>1.2</td>
<td>1M</td>
<td>1M</td>
<td>As above, no significant change</td>
</tr>
<tr>
<td>1.3</td>
<td>1M</td>
<td>1M</td>
<td>Crystals of slightly larger than above size. Crystals were apparently transparent</td>
</tr>
<tr>
<td>1.3</td>
<td>1.5M</td>
<td>1.5M</td>
<td>Crystals were large and thick having size $10 \times 8 \times 3 \text{ mm}^3$. Crystals were sufficiently transparent</td>
</tr>
<tr>
<td>&gt;1.3</td>
<td>0.5M to 1.5M</td>
<td>0.5M to 1.5M</td>
<td>Crystal size and transparency decreased</td>
</tr>
<tr>
<td>1.3</td>
<td>&gt;1.5M</td>
<td>1.5M</td>
<td>No formation of crystal. Only precipitation obtained</td>
</tr>
</tbody>
</table>
3.2 X-ray diffraction study

X-ray diffraction studies of the single crystals were carried out by using Enraf-Nonius single crystal CAD-4 diffractometer using graphite monochromatized MoKα (<1/128l = 0.7107 Å — radiation. About 25 reflections with θ, in the range of 2θ = 20-25° were used for the accurate determination of unit cell parameters using least-squares technique. The results are as under:

The crystal is Triclinic PI (or P111)

\[
\begin{align*}
\alpha &= 6.009(2) \text{ Å} \\
b &= 6.663(1) \text{ Å} \\
c &= 8.478(1) \text{ Å} \\
V &= 313.9(2.2) \text{ Å}^3 \\
\alpha &= 74.70(1)^\circ \\
\beta &= 74.27(2)^\circ \\
\gamma &= 81.02(2)^\circ
\end{align*}
\]

3.3 TGA Investigation

Cadmium oxalate crystals are found to contain three molecules of water of crystallization. Thermogravimetric analysis (shown in Fig. 4) indicates that it starts loosing weight of its water molecules at 85°C, becoming completely dehydrated at around 150°C where 21.2% weight loss suggests the loss of all its three H₂O molecules. The dehydrated CdC₂O₄ further starts decomposing at 300°C by loosing CO and CO₂ simultaneously yielding CdO as per scheme given below. The loosing of weight is complete at 340°C.

\[
\begin{align*}
\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O} \rightarrow \text{CdC}_2\text{O}_4 - 3\text{H}_2\text{O} \\
(\text{between 85 and 150°C}) \\
\text{CdC}_2\text{O}_4 \rightarrow \text{CdCO}_3 - \text{CO}_2 \\
\text{CdCO}_3 \rightarrow \text{CdO} \\
(\text{between 300 and 340°C})
\end{align*}
\]

According to the scheme, loss of 28.3% weight is very much in agreement to the experimental value of 27.4% from TGA curve.

The scheme reported earlier⁹ for decomposition of CdC₂O₄ yielding CdO as given by the equation

\[
\text{CdC}_2\text{O}_4 + \text{O}_2 \rightarrow 2\text{CdO}
\]

is found to be incorrect as per the present thermogravimetric analysis (shown in Fig. 4).

The weight loss of the grown sample is further supported by DSC (differential scanning calorimetry) curve during heating (shown in Fig. 5).
References